

ear region of the adsorption isotherm, the retention time and the peak width, defined as the first absolute moment μ_1 and the second central moment μ_2 , respectively, are functions of the quantities that characterize the chemical nature and texture of a solid packing [371-375]:

$$\mu_1 = f_1(K_s) \quad (175)$$

$$\mu_2 = f_2(K_s, k_a, e', D_{\text{int}}^{-1}) \quad (176)$$

where

K_s = partition coefficient in GSC,

k_a = adsorption coefficient,

e' = internal porosity of the particles with respect to the pore space (which, contrary to e_0 , the interparticle porosity, was not considered in eqns. (55) and (56),

D_{int} = effective diffusion coefficient of the separated substances in the pores of the solid.

Owing to the proportionality between K_s and the specific retention volume in GSC, V_s [eqn. (20)], the retention increases with increasing adsorption equilibrium constant, which in turn depends on the strength of the interaction of the compound to be adsorbed/desorbed with the solid phase. The differences in the K_s values for solutes with different chemical structures will be large, hence accomplishing the separation ($\mu_1 = f_1(K_s)$).

Strong adsorption invariably broadens the peak, as is apparent from eqn. (176) where K_s is involved, and as is confirmed by experience, i.e., it affects the efficiency and separability. A principal means of improving the peak width consists in the selection of adsorbents with a favourable pore size distribution, as μ_2 [eqn. (176)] depends on e' and on the reciprocal of the diffusion coefficient D_{int} in the pores of the solid. In narrow pores, e.g., with pore diameters 10 nm, the Knudsen diffusion is predominant, i.e., collisions of sample molecules with the pore walls take place more often than with other sample molecules or with molecules of the carrier gas. This special diffusion, the rate of which increases linearly with increasing pore diameter, is very slow (e.g., for n-hexane at 10 Torr, $D_{\text{Kn}} = 0.0202 \text{ cm}^2/\text{s}$, compared with the bulk diffusion coefficient for a hydrogen-n-hexane mixture of $D = 0.5148 \text{ cm}^2/\text{s}$ [375, 376]). In wide pores, i.e., with pore diameters > 200 nm, the rate of diffusion is independent of the pore diameter and the effective diffusion coefficient is proportional to the bulk diffusion coefficient.

To summarize, there are two essential characteristics of adsorbents by which they can be classified: their chemical structure and their geometrical structure.

5.1.1. Classification According to Chemical Structure

Based on the chemical nature of the adsorbent surface, different kinds of interactions with different sample molecules can occur. *Kiselev*, whose proposed classification [377, 378-379] has been generally accepted and applied, subdivides adsorbents into three groups (I-III) and adsorbates into four groups (A-D).

Adsorbents of type I

Non-specific adsorbents, which do not have any functional groups or ions on the surface and hence are not capable of specifically interacting with adsorbates. The interaction with all types of sample molecules A-D proceeds non-specifically. Adsorbents of this type are saturated hydrocarbons (in crystalline or solid polymer modification or as a layer on a suitable supporting adsorbent), graphite or rare gas crystals. The most important adsorbent of this type is graphitized thermal carbon black (GTCB) which in its adsorption properties approaches an ideally non-specific adsorbent when prepared or pre-treated in a suitable manner.

The adsorbed molecules are arranged in such way that they contact the highest possible number of surface atoms.

Owing to their structure, which is similar to that of graphite, the inorganic adsorbents boron nitride (BN), and sulphides of some metals (e.g., MoS_2) can be included in this group [379, 380].

Adsorbents of type II

Specific adsorbents exhibiting positive partial charges localized on the surface. In addition to the dispersion interactions that occur on any adsorbent independent of its type, specific interactions develop, resulting in an orientation and localization of the adsorbate molecules at the sites with the highest charge. Especially salts, in which the positive charge is concentrated on cations of small radius whereas the negative charge is distributed over a relatively large volume, belong to this type (e.g., BaSO_4). Zeolites, the cations of which have small atomic volumes, whereas the negative charge is distributed over the inner bonds of a large complex anion formed from AlO_4^- and SiO_4 tetrahedra, are also of this type [379].

However, the most significant representatives of this type are adsorbents with functional groups of protonated acids, such as hydroxylated silica gels, and with aprotic Lewis centres on the surface.

Sample molecules of type A (saturated hydrocarbons, rare gases) are adsorbed non-specifically, as only dispersion forces can become effective. Molecules of type B, C and D can be adsorbed specifically.

Type B include molecules with an electron density localized on some bonds or atoms: π -bonds (unsaturated and aromatic hydrocarbons); functional groups, the atoms of which exhibit unshared electron pairs (ethers, ketones, tertiary amines, pyridine, nitriles); high quadrupole moments (N_2 molecules)

The interaction between type B adsorbates and type II adsorbents occurs between the centres of higher electron density (sample molecule) and the positive charge of the adsorbent (for example, the acidic proton of hydroxylated silica gel or an appropriate cation (Li, Na, Mg, Ca) in zeolites or aprotic Lewis centre (Al, B) on the surface).

Type C molecules have a localized positive charge on a metal atom and the excess of the electron density is distributed over adjacent bonds (organometallic compounds). Because of the high reactivity of many organometallic compounds and of the risk of chemisorption, there have been only a few investigations of this interaction.

Type D molecules contain peripheral functional groups (OH, NH, etc.), the electron density of which is increased on one of the atoms (O, N) and diminished on the other (H). This group includes water, alcohols and primary and secondary amines. The specific interactions of type D adsorbates with type II adsorbents mainly involve forces between the positive charge centres of the adsorbent and the lone electron pairs of the O or N atoms of the sample molecules.

Adsorbents of type III

Specific adsorbents bearing centres of higher electron density on the surface. To this group belong polymers such as polyacrylonitrile, copolymers of vinylpyridine and divinylbenzene and polymers with $\text{C}=\text{O}$ and $-\text{O}-$ groups on the surface. Porous polymers based on styrene-ethylvinylbenzene, cross-linked with divinylbenzene, varied by applying different polymerization initiators with various functional groups, may also be included in this group, even if non-specific dispersion forces preponderate. Type III adsorbents include also crystal surfaces formed by anions, and especially chemically modified adsorbents or non-specific adsorbents covered by a dense monolayer of suitable substances, hence creating negative charge centres on the surface.

Adsorbents of type III interact non-specifically with adsorbates of type A and specifically

with types such as B, C and D by forces between the negative charge on the adsorbent's surface and the positive charge of the metal atom (C) or of the functional group's (OH, NH) proton (D) or of the dipole or an induced dipole (B).

5.1.2. Classification According to Geometrical Structure

We had stated that the geometry of the adsorbents influences especially the capacity term in eqn. (100). Hence the surface area should be as high as possible in order to increase this term. However, there are serious reservations. Increasing the surface area means either increasing the dispersity (with the consequence of an increase in heterogeneity due to the increasing contact points between the particles) or narrowing the pore diameters (with the disadvantage of Knudsen diffusion). The outcome of numerous investigations in this field, among which especially the work of *Kiselev* should be given prominence, has been that difficulties of this kind, having retarded the development of GSC for a long time, have been surmounted [379].

The role of the surface area can be derived from basic equations in Chapter 2. For infinitely small (zero) samples, the net retention volume V_N , under equilibrium conditions, is equal to the Henry constant of the adsorption equilibrium [379]:

$$V_N = K_H = \lim_{n_{ads} \rightarrow 0} \left(\frac{n_{ads}}{c} \right) \quad (177)$$

where c is the concentration of the sample in the gas phase. If we consider the total surface area of the adsorbent in the column, $m_A S_A$, where m_A = weight of the adsorbent and S_A = specific surface area of the adsorbent, we obtain (from eqns. (11) and (20)), neglecting the temperature,

$$V_S = \frac{V_N}{m_A S_A} = K_S,$$

which is the adsorption coefficient (or the Henry constant referred to unit surface area of the adsorbent).

From $V_N = K_H$ we obtain the correlation of both constants K_H and K_S with the geometrical parameter:

$$V_N = K_H = m_A S_A V_S = m_A S_A K_S. \quad (178)$$

Hence V_N , the net retention volume, can be influenced by both the column parameters (weight of the adsorbent m_A) and the geometrical characteristic of the adsorbent, its specific surface area S_A . K_S , however, can be influenced by the chemical nature and structure of both the interacting adsorbent and adsorbate, expressed by analogy with eqn. (189a) as the partial molar adsorption enthalpy [381]:

$$\frac{d \ln K_S}{dT} = \frac{\Delta H_A}{RT^2}. \quad (179)$$

As ΔH_A , the partial molar adsorption enthalpy, changes only slightly with the temperature, we can write [379]

$$\ln K_S \approx -\frac{\Delta H_A}{RT} + \frac{\Delta S_A}{R} + 1 \quad (180)$$

or

$$K_S \approx \exp \left[\frac{\Delta S_A}{R} + 1 \right] \exp \left[\frac{-\Delta H_A}{RT} \right], \quad (180a)$$

where ΔS_A = partial molar adsorption entropy of the adsorbate for the transition from the standard state of the gas volume with concentration c^0 into the standard adsorbate state with an adsorption concentration Γ^0 .

Eqn. (180a) shows the exponential dependence of K_s on temperature, the third essential parameter in GSC, in addition to the adsorbent's chemical structure and geometrical structure. Eqns. (178) and (180a) demonstrate that even adsorbents with small specific surface areas permit the separation of weakly adsorbable gases, provided that the column temperature is decreased accordingly, hence increasing K_s and thus also its product with the surface area, $m_A S_A K_s$ [379]. The alternative, or better for completion when separating low boiling gases, is the use of adsorbents with small particle diameters and/or fine pores, hence increasing S_A and $m_A S_A$.

Kiselev and Yashin [377] classified adsorbents geometrically as follows.

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| Type 1 | Non-porous adsorbents
Crystalline products with a smooth surface (sodium chloride, graphitized thermal carbon black, BN, MoS ₂)
S_A values 0.1–12 m ² /g. |
| Type 2 | Uniformly porous adsorbents with wide pores
Silica gels with pore diameters between 10 and 200 nm (but each silica gel product with narrowly distributed pore diameters!)
(Porasil, Spherasil) and phases bonded chemically on silica gel
(Durapak, etc.) as also some wide-pore styrene-divinylbenzene polymers (pore diameters 20–400 nm). |
| Type 3 | Uniformly porous adsorbents with narrow pores
Molecular sieves (zeolites), carbon molecular sieves, porous glasses, porous polymers. Pore diameters 10 nm. |
| Type 4 | Irregularly porous adsorbents
Active charcoal, alumina. Owing to the geometrical (and chemical!) heterogeneity [the pore diameters range from 2–20 nm (transition pores) up to >200 nm (macropores)], such adsorbents are not appropriate for GSC (with the exception of their use as enrichment materials), even though they were widely applied in the early years of gas chromatography. |

This classification is based on the existence and size of the pores. Porous adsorbents differ from non-porous solids by a void structure shaped from a system of pores. This structure can be characterized, independent of the chemical composition of the adsorbent, by the following quantities [382]:

- Specific surface area S_A (geometric size of the pore wall area per gram of adsorbent).
- Specific pore volume V_p (total pore volume per gram of adsorbent).
- Mean pore diameter d_{50} (average diameter of 50% of the pores; this value is identical with the maximum frequency only for a homogeneous pore size distribution).
- Pore size distribution (distribution function $d(V_p)/d(d_{50})$).

They can be determined by gas chromatography [381], mercury porosimetry and reversed size exclusion chromatography [383]. Important for porous adsorbents is the ratio of their pore diameters to the diameters of the adsorbate molecules. If this ratio is high, i.e., the pore diameters are much larger than the molecule diameters, then the adsorption equilibrium is established rapidly. If the pore diameters are similar in size to the adsorbate molecules, then the adsorption rate depends on both the pore shape and the size of the molecules. In narrow pores the adsorbed molecule may interact with surface atoms of the opposite pore walls, and the exchange of molecules with the mobile phase is delayed. Hence the adsorption behaviour